



# Reaction Microarrays

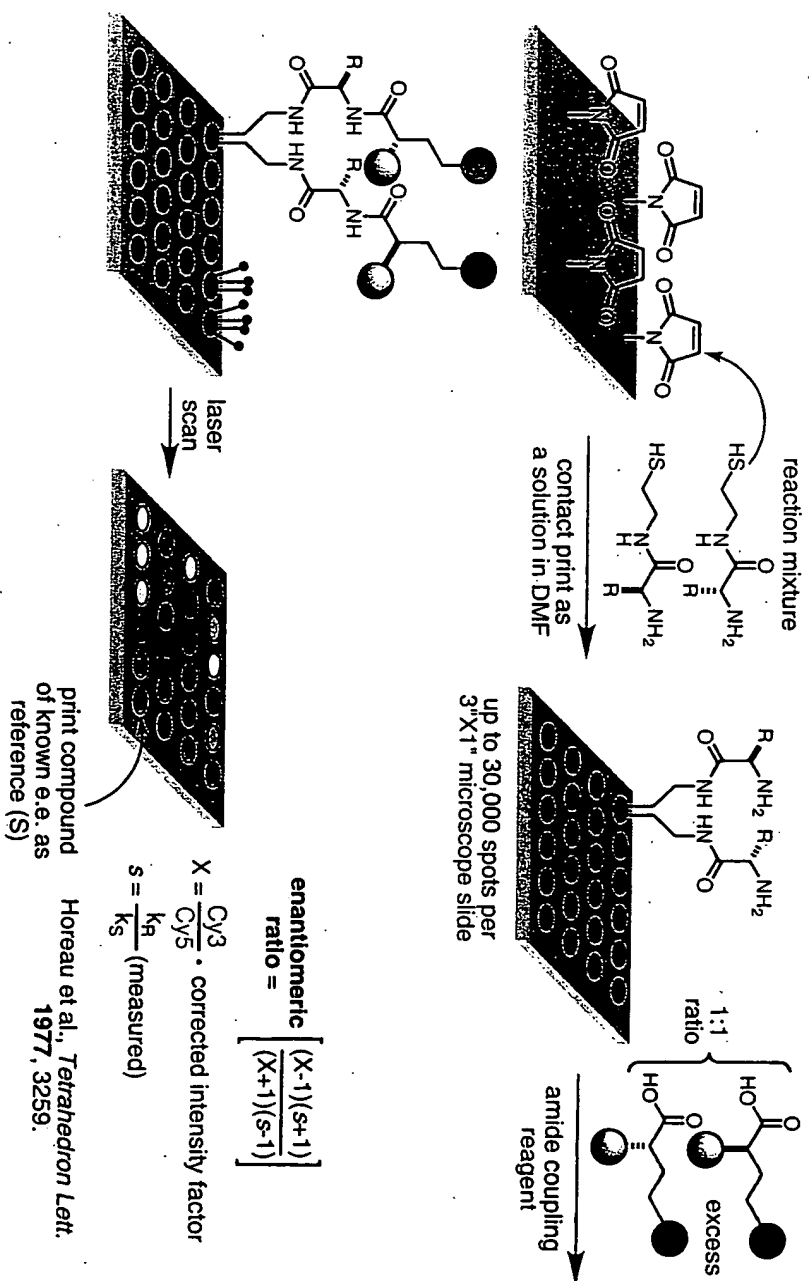
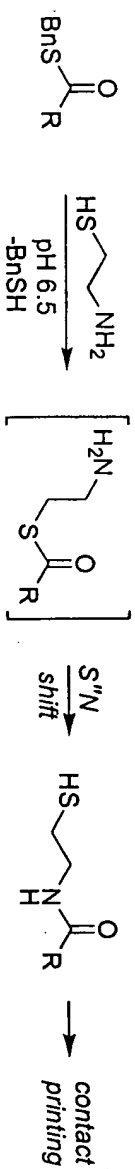


Figure 2

## Chemical ligation as a chemoselective method of thiol incorporation for printing



## Substrates for reaction microarrays

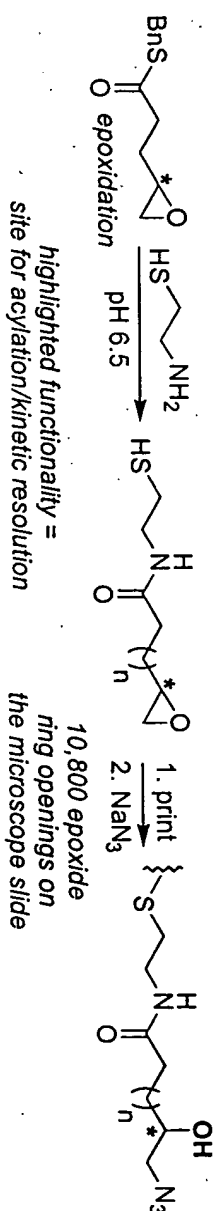
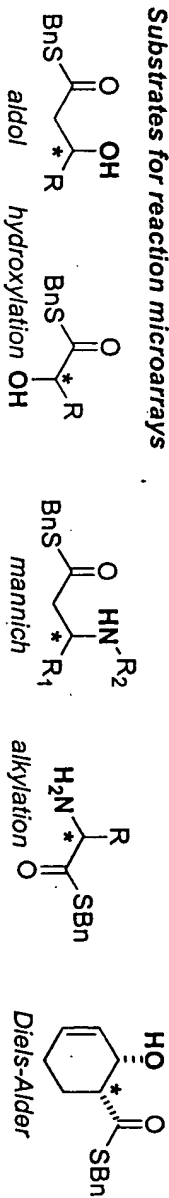
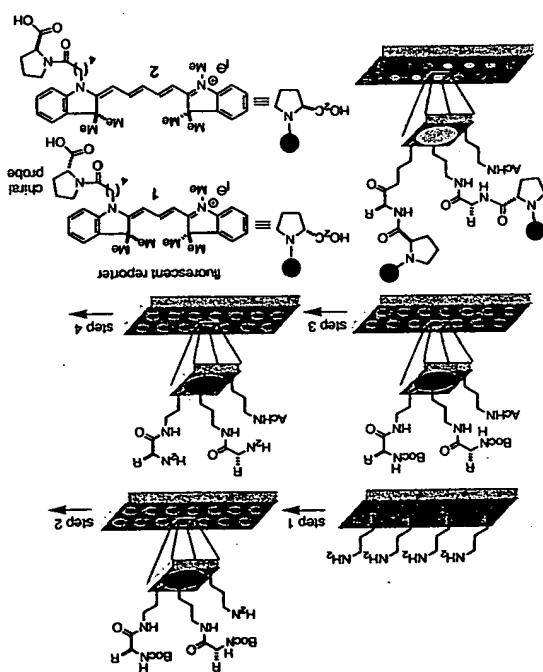
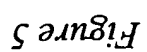


Figure 3

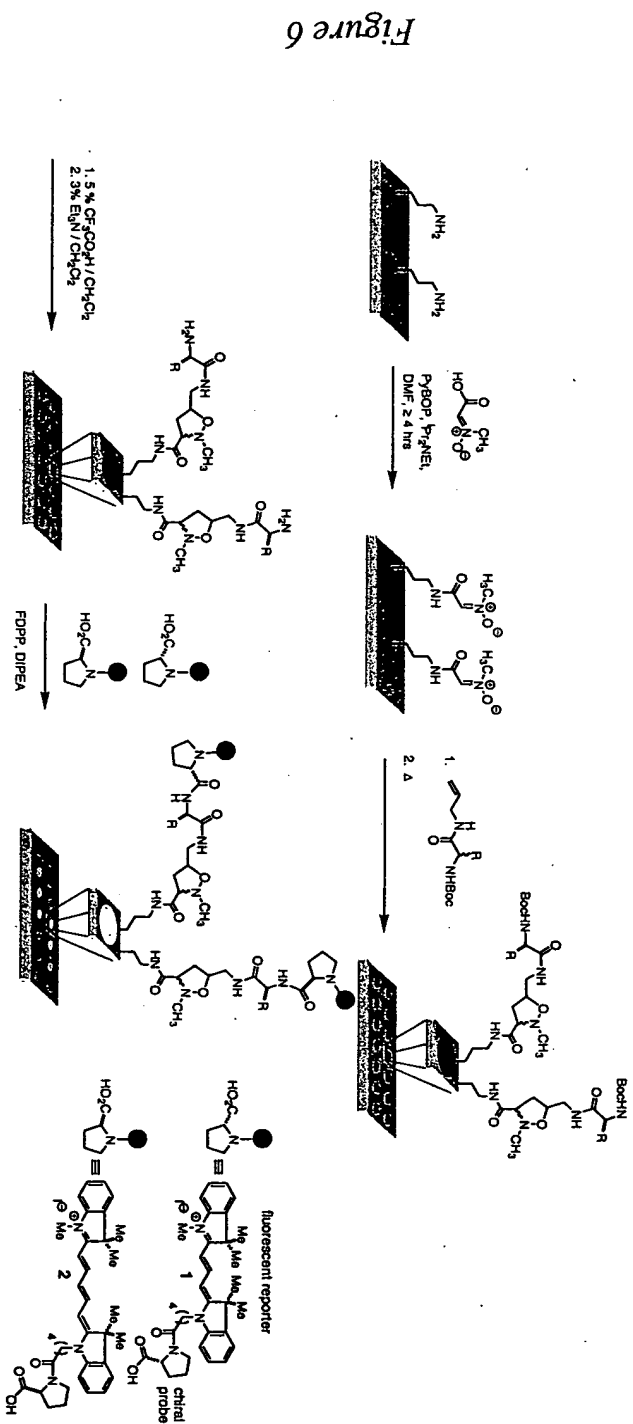


Reagents and conditions: step 1)  $\text{BooCHNCH(R)(CO}_2\text{H)}$ ,  $\text{PyAOP}$ ,  $\text{Pr}_2\text{NEt}$ ,  $\text{DMF}$ ; step 2)  $\text{Ac}_2\text{O}$ , pyridine; step 3) 10%  $\text{CF}_3\text{CO}_2\text{H}$  and 10%  $\text{Et}_3\text{SiH}$  in  $\text{CH}_2\text{Cl}_2$ , then 3%  $\text{Et}_3\text{N}$  in  $\text{CH}_2\text{Cl}_2$ ; step 4) pentafluorophenyl diphenylphosphinate,  $\text{Pr}_2\text{NEt}$ , 1:1 mixture of 1 and 2,  $\text{DMF}$ ,  $-20^\circ\text{C}$ .

Figure 4



Attachment of amino acids as their allyl amides to nitrene-functionalized microspheres



# Synthesis of Indocarbocyanine and Indodicarbocyanine Fluorophores

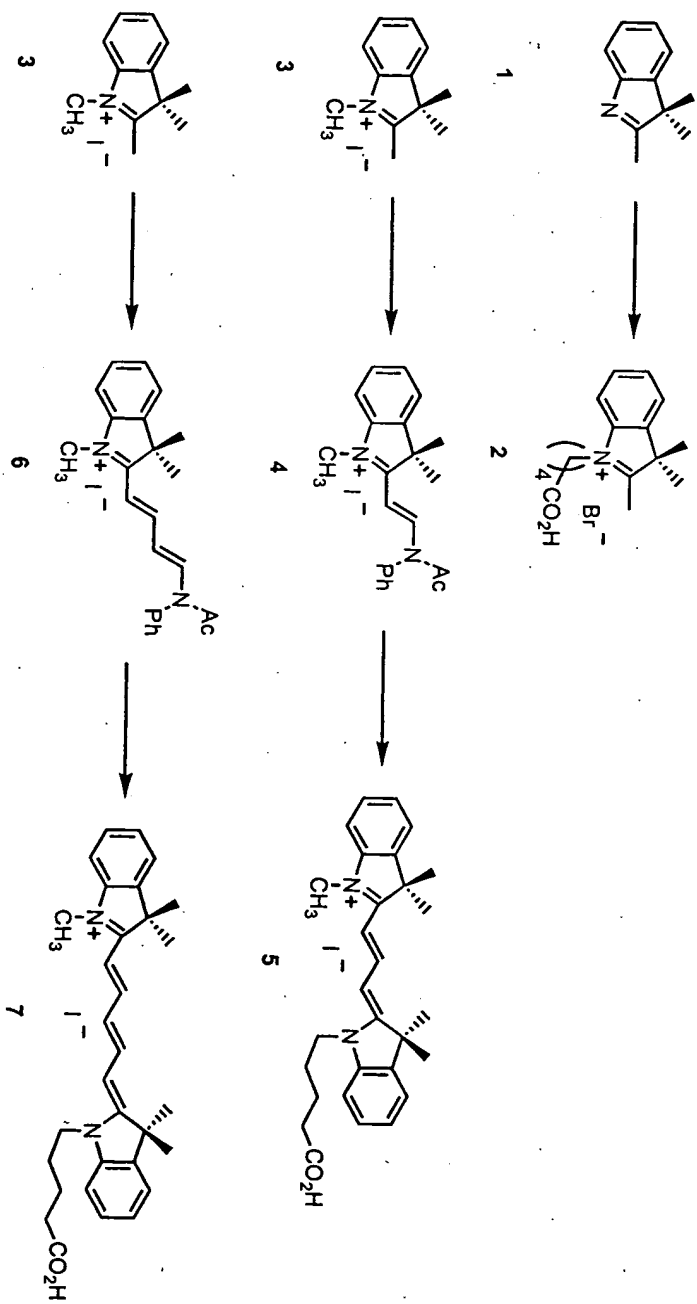


Figure 7

# Synthesis of Cy3 Fluorophore Conjugates by <sup>t</sup>Bu-Protected Amino Acids

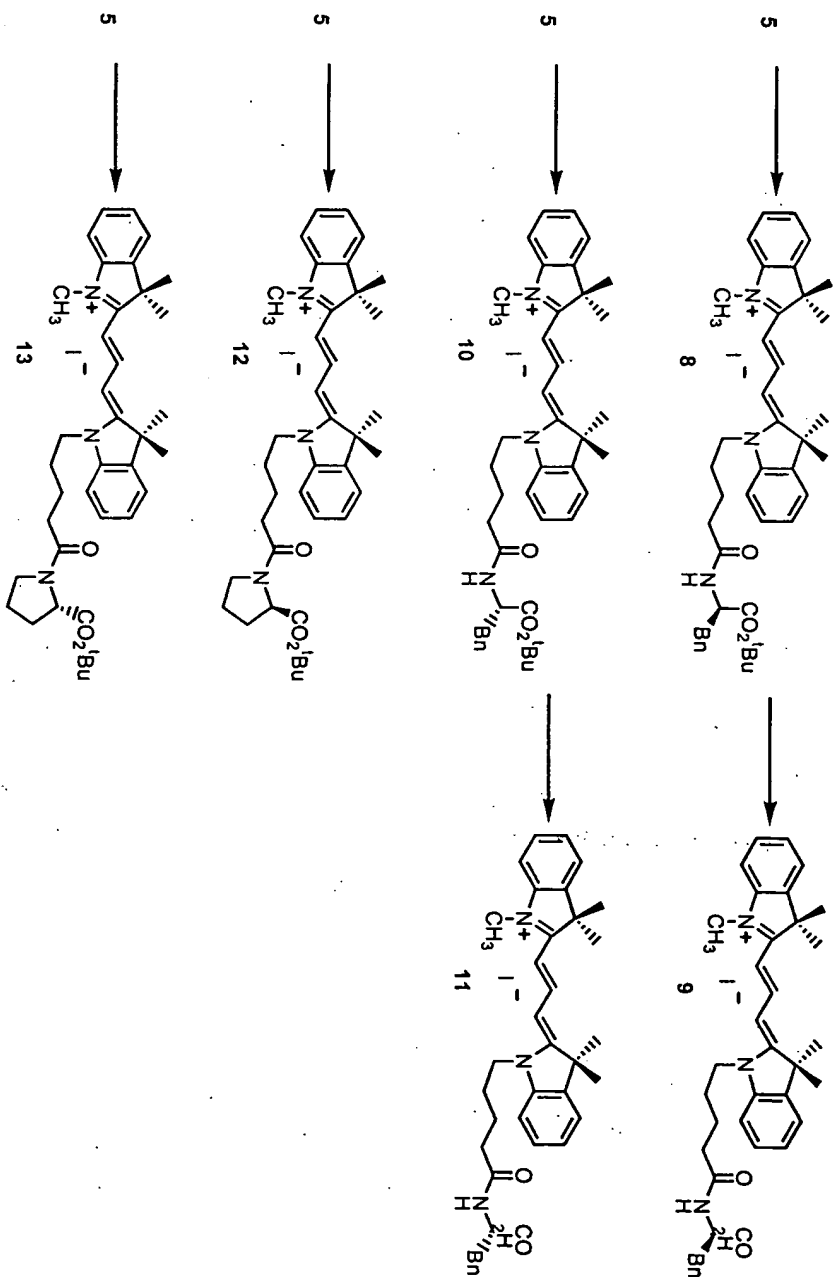


Figure 8



# Synthesis of Cy5 Fluorophore Conjugates by <sup>t</sup>Bu-Protected Amino Acids

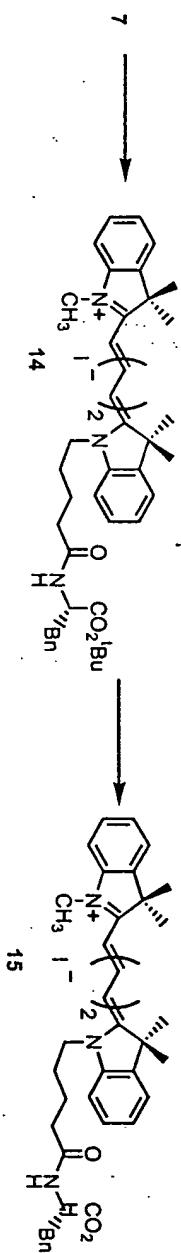
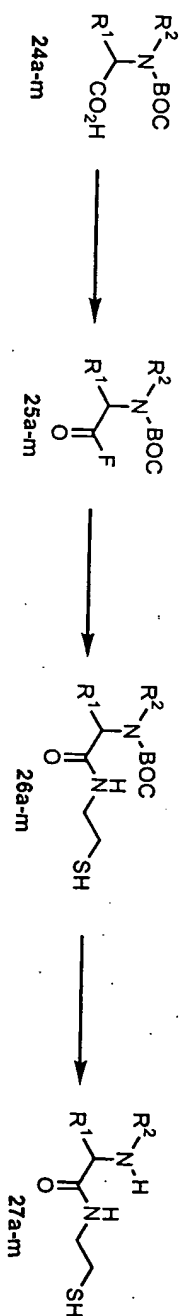


Figure 9

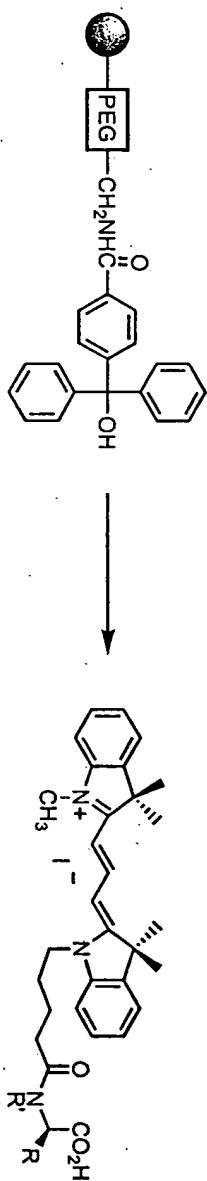
# Synthesis of Amino Acid Substrates for Printing



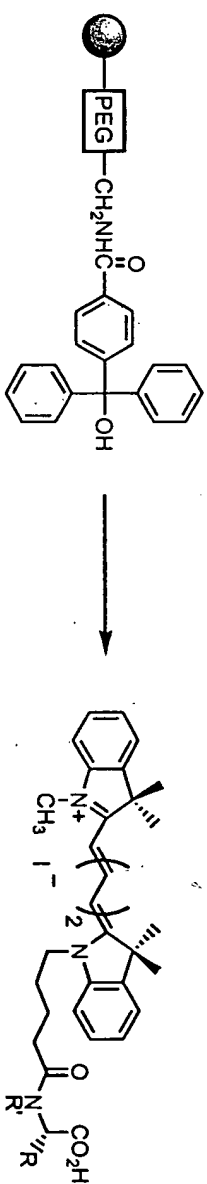
- <sup>a</sup> R<sup>1</sup> = R<sup>2</sup> = H  
 (R)-b R<sup>1</sup> = Me, R<sup>2</sup> = H  
 (S)-c R<sup>1</sup> = Me, R<sup>2</sup> = H  
 (R)-d R<sup>1</sup> = CH<sub>2</sub>CH<sub>2</sub>, R<sup>2</sup> = CH<sub>2</sub><sup>-</sup>  
 (S)-e R<sup>1</sup> = CH<sub>2</sub>CH<sub>2</sub>, R<sup>2</sup> = CH<sub>2</sub><sup>-</sup>  
 (R)-f R<sup>1</sup> = <sup>i</sup>Pr, R<sup>2</sup> = H  
 (S)-g R<sup>1</sup> = <sup>i</sup>Pr, R<sup>2</sup> = H  
 (R)-h R<sup>1</sup> = <sup>t</sup>Bu, R<sup>2</sup> = H  
 (S)-i R<sup>1</sup> = <sup>t</sup>Bu, R<sup>2</sup> = H  
 (R)-j R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 (S)-k R<sup>1</sup> = Ph, R<sup>2</sup> = H  
 (R)-l R<sup>1</sup> = Bn, R<sup>2</sup> = H  
 (S)-m R<sup>1</sup> = Bn, R<sup>2</sup> = H

Figure 10

# Solid Phase Synthesis of Cyanine-Amino Acid Conjugates



- 9 R = Bn, R' = H
- 16 R = CH<sub>2</sub>CH<sub>2</sub>, R' = CH<sub>2</sub>
- 17 R = Me, R' = H
- 18 R = <sup>i</sup>Pr, R' = H
- 19 R = <sup>t</sup>Bu, R' = H
- 20 R = Cyclohexylmethyl, R' = H



- 21 R = CH<sub>2</sub>CH<sub>2</sub>, R' = CH<sub>2</sub>
- 22 R = Me, R' = H
- 23 R = <sup>i</sup>Pr, R' = H

Figure 11

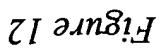
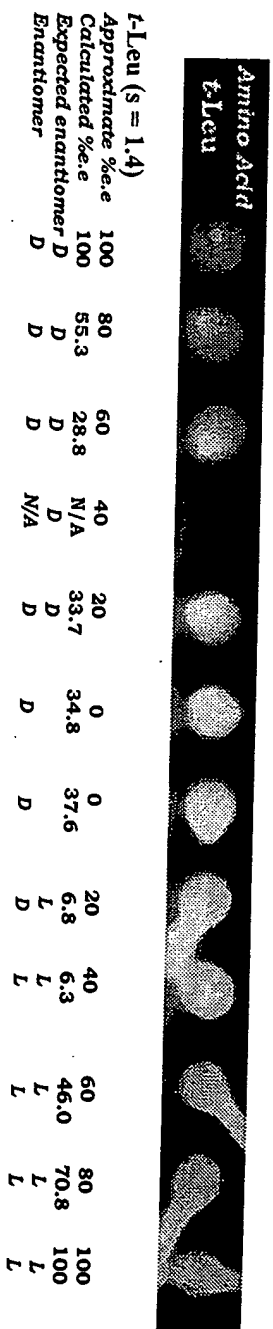


Figure 13



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